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# Molecular dynamics of a ferroelectric smectogen in its smectic phases by means of $^{2}$H NMR spectroscopy

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In this work the dynamic behaviour of the ferroelectric liquid crystal (-)-($S$)-[4-(2-methylbutyloxycarbonyl)phenyl] 4-*n*-heptylbiphenylcarboxylate (MBHB) in its smectic A (SmA), unwound chiral smectic C (uSmC*) and chiral smectic C (SmC*) phases has been studied by means of $^{2}$H NMR spectroscopy. Zeeman ($T_{1Z}$) and quadrupolar ($T_{1Q}$) spin-lattice relaxation times have been analysed to extract dynamic parameters (diffusion coefficients and activation energies). The small step rotation diffusion model in the uniaxial approximation has been used to describe overall spinning and tumbling motions, and the strong collision model to describe the internal reorientations of the aromatic fragment. Relaxation data in the SmC* phase have been analysed by using a theoretical approach. The dynamic features obtained in the smectic phases of this mesogen are here presented and discussed in comparison with the results obtained in other ferroelectric liquid crystals, focusing on the fast regime of motions.

## 1. Introduction

Ferroelectric liquid crystals (FLCs) formed by molecules containing one or more chiral carbons represent a very interesting class of new materials because of their possible technological applications. Some of their properties derive directly from molecular features and, among them, molecular dynamic properties are very important from the chemical physics point of view [1].

Besides collective fluctuations of the director, the molecular motions in thermotropic liquid crystals can be roughly divided into 'translational diffusion' and 'reorientational' processes of the molecule itself, relative to the symmetry axes of the mesophase. Two fundamental assumptions are the basis of the description of the stochastic processes in liquid crystalline systems. Firstly, the translational and orientational motions are considered decoupled, thus treated independently. Secondly, less evident, the overall molecular motions are often assumed separated from conformational internal ones, even though both usually take place on a similar time scale, giving rise to a quite complicated molecular dynamics mechanism. Since the liquid crystalline molecules are individually involved in translational motions, they show different features depending on the symmetry of the phase. At the same time, groups of molecules also experience collective motions, in which the spatial average orientation of molecules fluctuates slowly compared with the much faster reorientational motions of the single molecules.

In this context, nuclear magnetic resonance is a very powerful spectroscopic technique, not only because it can cover a wide range of time scale, occurring to different nuclei and nuclear interactions, but also because it provides the possibility of using these different interactions to obtain specific information, even localized on particular sites of the molecule.

Deuterium represents the nucleus most widely used to obtain dynamic information on LC systems [2, 3]. On the other hand, $^{1}$H and $^{13}$C nuclei [4, 5] could also give a wealth of information. Among the different deuterium relaxation times [6], each defining specific dynamic windows suitable to indicate different motions, the two spin-lattice relaxation times, $T_{1Z}$ and $T_{1Q}$, are particularly sensitive to motions with correlation times of the same order of magnitude as the inverse of the Larmor frequency, i.e. in the range of $10^{-11}$–$\tau_c$–$10^{-7}$ s in the case of a high magnetic field ($\mathbf{B}>5$ T).

$^{2}$H NMR spin-lattice relaxation times have been widely used to obtain detailed dynamic information in uniaxial LC mesophases formed by uniaxial molecules [6]. Indeed, several theories have been developed that

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link the spectral densities to dynamic parameters (such as diffusion coefficients and activation energies) describing the individual overall molecular, internal and collective motions occurring in these phases over a broad timescale. Even though relaxation times can also be measured in tilted smectic phases, there are several difficulties in linking them to the dynamic parameters [7]; for this reason quantitative analyses of relaxation times in such phases have only been reported recently [8, 9]. These difficulties are both theoretical and experimental and are due either to the phase biaxiality or to the dependence of the relaxation times on the polar angles defining the position of the local phase director with respect to the external magnetic field [10]. On the one hand theoretical models taking into account phase biaxiality are quite complex [11, 12], while on the other such a model would require an unavailably large set of experimental data.

In this work we present a different case from other papers in the literature [8, 9], since the ferroelectric sample, (-)-(*S*)-[4-(2-methylbutyloxycarbonyl)phenyl] 4-*n*-heptylbiphenylcarboxylate (MBHB), shows a smectic C* phase unwound by the magnetic field (at 7 T), called unwound SmC* phase (uSmC*). The dynamic behaviour experimentally found in the SmA, uSmC* and SmC* phases of this mesogen by means of $^2$H NMR relaxation is here presented and discussed. This case represents a further test for the theoretical approach developed in the SmC* phase by Domenici and co-workers [8] and an original case due to the presence of a transition between the unwound SmC* and the SmC* phases.

## 2. Theory

The relationships that link the spin-lattice relaxation times $T_{1Z}$ and $T_{1Q}$ to the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ are [6]:

$$\frac{1}{T_{1Z}(\Omega)}=J_1(\omega_0,\Omega)+4J_2(2\omega_0,\Omega) \tag{1}$$

and

$$\frac{1}{T_{1Q}(\Omega)}=3J_1(\omega_0,\Omega) \tag{2}$$

where $\omega_0$ is the Larmor frequency and $\Omega=(\theta,\ \phi)$ indicates the polar angles of the phase director in the laboratory frame defined by the external magnetic field. Several models have been proposed to interpret the spectral densities in uniaxial phases at $\theta=0$ (i.e. with the phase directors aligned to the external magnetic field) in terms of dynamic parameters of individual internal and overall molecular motions. Using the small step rotation model developed by Nordio *et al.* [13], Vold and Vold [14], and later Tarroni and Zannoni [15], in the uniaxial approximation for the overall molecular reorientations, superimposed with the strong collision model [16] for the internal motions, the following equation can be derived for the spectral densities of the *i*-th deuteron (in the Vold notation):

$$J^i_{mL}(n\omega_0)=\frac{3\pi^2}{2}\left(v_q\right)^2\sum_{m_M=-2}^{2}\sum_{m_R=-2}^{2}c_{m_L,m_M}\left[d^2_{m_R,0}\left(\beta_{i,Q_i}\right)\right]^2 \left[d^2_{m_M,m_R}\left(\beta_{M,i}\right)\right]^2 \sum_j a^{(j)}_{m_L,m_M}\frac{\left(\tau^{(j)}_{m_L,m_M}\right)^{-1}+(1-\delta_{mR})D_i}{(n\omega_0)^2+\left[\left(\tau^{(j)}_{m_L,m_M}\right)^{-1}+(1-\delta_{mR})D_i\right]^2} \tag{3}$$

where the autocorrelation functions for the overall molecular motions have been expressed as a sum over $j$ of decreasing exponential functions with time constants $\tau^{(j)}_{mL,mM}$, see equation (4); the coefficients $a^{(j)}_{mL,mM}$, $b^{(j)}_{mL,mM}$ and $c_{mL,mM}$, have been calculated by Volds as a function of the principal order parameter $S_{zz}$ for a Maier–Saupe potential [17], $v_q$ is the quadrupolar coupling constant; $d^2_{r,s}$ are the reduced Wigner matrices; $\beta_{i,Qi}$ is the angle between the C-D bond and the axis about which the internal rotation takes place; $\beta_{M,i}$ is the angle between this axis and the molecular long axis, $z$ and $D_i$ is the diffusion coefficient relative for internal motion of the corresponding fragment. Here $S_{zz}$ is the nematic order parameter of the long molecular axis. The correlation times $\tau^{(j)}_{mL,mM}$ are expressed in terms of the diffusion coefficients $D_{//}$ and $D_{\perp}$, the principal components of the diffusion tensor diagonalized in a molecular frame, describing the molecular spinning and tumbling motions, respectively:

$$\frac{1}{\tau^{(j)}_{m_L,m_M}}=\frac{6D_{\perp}}{b^{(j)}_{m_L,m_M}}+m^2_M\left(D_{//}-D_{\perp}\right). \tag{4}$$

When a tilted smectic phase is considered, $\theta$ is different from zero and the relaxation times are in principle dependent on both the polar angles $\theta$ and $\phi$. On the other hand, an analysis of experimental relaxation times in the SmC* phase on this basis is impossible for both experimental and theoretical reasons.

For example, in a chiral smectic C* phase, the phase director describes a helicoidal structure along the normal to the smectic planes ($z$-axis, parallel to the magnetic field), i.e. the tilt angle $\theta$ always remains fixed, while the azimuthal angle $\phi$ assumes different values depending on the $z$-coordinate. In an aligned SmC* phase, the helical pitch is along the external magnetic field. However, equivalent deuterons of different molecules corresponding to different smectic planes and, therefore, different $\phi$ values, give exactly the same quadrupolar doublet in the $^2$H NMR spectrum. Consequently, only one, average relaxation decay can be recorded for all the equivalent deuterons of the phase.

Even if different experimental values for the relaxation times could be obtained for different $\phi$ values, no suitable theories would be actually available to analyse them in terms of dynamic parameters. An assumption that allows us to treat the experimental relaxation times in tilted smectic phases, consists of considering them independent from the azimuthal angle $\phi$. This assumption, that could seem too drastic, is indeed supported by the experimental evidence of a mono-exponential decay for all the $^2$H spin-lattice measurements performed so far on tilted smectic phases, indicating that, if the $\phi$-dependence existed, it would nevertheless be so small as to be undetectable. Two recent studies on the SmC* phase of chiral smectogens, 10B1M7 and 11EB1M7, have indeed confirmed such an assertion [18, 19]. It is therefore safe to ignore the biaxial spectral densities in the following equations. By neglecting the $\phi$-dependence the following equations can be derived [20]:

$$
\begin{aligned}
J_1(\omega,\theta) = {} & \left(\frac{3\cos^2\theta\sin^2\theta}{2}\right)J_0(\omega,0) \\
& +\left(\frac{1-3\cos^2\theta+4\cos^4\theta}{2}\right)J_1(\omega,0) \\
& +\left(\frac{1-\cos^4\theta}{2}\right)J_2(\omega,0)+ \\
& -\sqrt{6}\left(\cos^2\theta\sin^2\theta\right)J_{2,0}(\omega,0) \\
& -\left(\frac{1-5\cos^2\theta+4\cos^4\theta}{2}\right)J_{1,-1}(\omega,0) \\
& -\left(\frac{1-\cos^2\theta}{2}\right)^2 J_{2,-2}(\omega,0)
\end{aligned}
\tag{5}
$$

$$
\begin{aligned}
J_2(\omega,\theta) = {} & \left(\frac{3\left(1-\cos^2\theta\right)^2}{8}\right)J_0(\omega,0)+\left(\frac{1-\cos^4\theta}{2}\right) \\
& J_1(\omega,0)+\left(\frac{1+6\cos^2\theta+\cos^4\theta}{8}\right)J_2(\omega,0)+ \\
& +\sqrt{6}\left(\frac{1-\cos^4\theta}{4}\right)J_{2,0}(\omega,0)+\left(\frac{1-2\cos^2\theta}{2}\right) \\
& J_{1,-1}(\omega,0)+\left(\frac{1-\cos^2\theta}{8}\right)J_{2,-2}(\omega,0).
\end{aligned}
\tag{6}
$$

Equations (5) and (6), also used in angular dependence studies [21] link the experimental spectral densities $J_1(\omega, \theta)$ and $J_2(\omega, \theta)$ to the spectral densities at $\theta=0$, to be used within the theoretical models. The spectral densities measured by the Jeener–Broekaert experiment for each type of deuteron at a given temperature are only two [$J_1(\omega_0, \theta)$ and $J_2(2\omega_0, \theta)$], and therefore the six spectral densities at $\theta=0$, even without the biaxial spectral densities [$J_1(0, 0)$, $J_2(0, 0)$, $J_1(\omega_0, 0)$, $J_2(\omega_0, 0)$, $J_1(2\omega_0, 0)$ and $J_2(2\omega_0, 0)$], cannot be directly determined from equations (5) and (6). The neglect of biaxial spectral densities is justified based on a recent experimental finding of zero biaxial ordering in the SmC* phase of 10B1M7 [22]. A global target approach is used, which assumes an Arrhenius behaviour for the various diffusion coefficients $D_k(T)=D_k^{\infty}\exp\left(-E_a^k/kT\right)$, the label $k$ indicating the type of motion), the best values of the parameters $D_k^{\infty}$ and $E_a^k$ can be determined by applying a suitable non-linear least-squares fitting procedure [23].

## 3. Experimental

### 3.1. *The sample*

The sample under investigation was the ($S$)-[4-(2-methylbutyloxycarbonyl)phenyl] 4′-$n$-heptylbiphenyl carboxylate (MBHB). A single isotopomer of MBHB, deuterated on the biphenyl fragment (MBHB-$d_8$), was synthesized [24] to perform deuterium NMR studies (see figure 1).

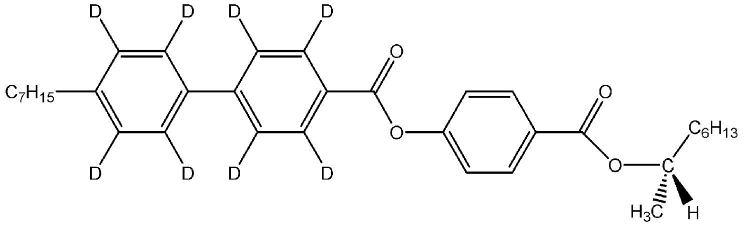

Figure 1. Molecular structure of the ferroelectric smectogen MBHB-$d_8$.

MBHB presents several mesophases on cooling a sample from the isotropic phase, as reported in the following scheme (DSC): I 435.5 SmA 367 SmC* 326 SmI* 310 Cr (K). A peculiarity of this sample is the unwinding of the SmC* helix (at $\mathbf{B}_0=7.05$ T), as discussed in detail in [25], so that the following phase behaviour was observed at this field in our case by $^2$H NMR: I 434 SmA 365 uSmC* 351 SmC* 326 SmI* 310 Cr (K).

### 3.2. *$^2$H NMR*

$^2$H Zeeman ($T_{1Z}$) and quadrupolar ($T_{1Q}$) spin-lattice relaxation times were recorded by means of a broadband version [26] of the Jeener–Broekaert pulse sequence [27]. The relaxation measurements were recorded on a VarianVXR-300 spectrometer working at 46 MHz. The samples were microscopically aligned within the magnet by slow cooling from the isotropic phase and the spectra were recorded allowing 10 minutes for thermal equilibration. The temperature was stable within 0.2 degrees. Orientational order and magnetic field effects on the unwinding of the chiral smectic C helix are reported in [28] and [25], respectively. Details of the relaxation measurements and the partial analysis in the SmA phase have appeared in [28].

### 3.3. *Data analysis*

All relaxation data are analysed using a modified version of the CAGE package [23], including the treatment of the biaxial phase according to the approach developed by this group [8].

## 4. Results

The analysis of the relaxation times, measured for the biphenyl deuterons of MBHB at a single frequency, was previously reported in the SmA and uSmC* phases [28]. In fact, in the uSmC* phase the helix is unwound and the phase director **n** is aligned with the external magnetic field, whilst the smectic layers are tilted, and therefore this could be treated as a uniaxial phase (see figure 2). However, this analysis was carried out without fixing any parameters, and therefore getting a substantial uncertainty for the coefficient for the tumbling motion, $D_\perp$.

In the present work, the analysis was repeated in the SmA and uSmC* phases, and extended to the SmC* phase, by fixing the ratio $D_{//}/D_\perp$ to the value of 5 on the basis of the Perrin model [29]. In fact, when few data are available, it is well known that the fitting procedure is not self-consistent, giving rise to several best-fitting sets of parameters instead of one. In this case, different values of $D_\perp$ are found to give a good fitting of the experimental data, thus giving a substantial uncertainty in the parameter describing the tumbling motion. The Perrin model allows us to calculate the ratio between $D_{//}$ and $D_\perp$ starting from the values of the main axes of the principal momentum of inertia. To this aim, after optimizing the molecular structure of MBHB using standard Monte Carlo methods, we evaluated the principal axes of the momentum inertia tensor and used them to compute the ratio $D_{//}/D_\perp$. In this way, we could obtain a self consistent set of parameters from best-fitting the data.

In particular, two separate global fitting analyses were performed, the first in the SmA and uSmC* phases and the second in the SmC* phase, by using the small step rotation diffusion model to describe the overall molecular motions and the strong collision model for the internal rotations. Totals of 30 and 12 experimental points (two spectral densities measured at 15 and 6 different temperatures, respectively) were used to determine four parameters (pre-exponential factor and activation energy for molecular spinning and internal biphenyl ring rotation) in each case.

The uSmC* phase has not been treated separately because of the lack of a large set of experimental data and because the phase is stable in only a short range of temperature. Moreover, the analysis of relaxation times in this phase can be done together with the SmA phase, considering that they are both uniaxial phases. In fact, we assume that the layer normal direction with respect to the external magnetic field, which is different in the SmA and uSmC* cases, is not relevant for the relaxation analysis.

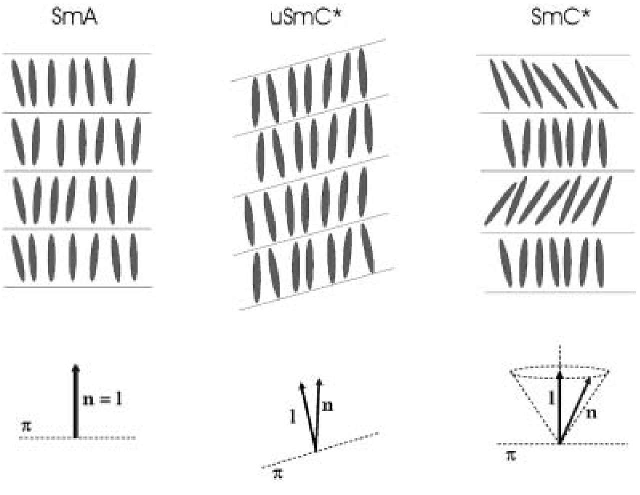

Figure 2. Schematic structure of (*a*) Smectic A, (*b*) unwound SmC* and (*c*) SmC* phases in a magnetic field (assumed to be in the vertical position). Vectors **n**, **l** and **π** indicate the phase director, the normal to the smectic plane and the smectic plane, respectively.

The order parameters and tilt angle values needed for the relaxation time analysis were taken from the results obtained from analysing the $^{2}$H quadrupolar splittings [24]: $S_{zz}$ (relative to the phase director) ranges from 0.62 to 0.75 within the SmA and uSmC* phases, and from 0.75 to 0.79 within the SmC* phase. The tilt angle $\theta$ was found to increase slightly on increasing the temperature from 7.4° to the limiting value of 10.3° within the SmC* phase. Values of 60° and 0° were taken for $\beta_{i,Qi}$ and $\beta_{M,i}$, respectively [28]. It should be noted that the long molecular axis of MBHB has been assumed to be colinear with the *para*-axis of the byphenyl fragment, and that the *z*-direction mentioned in the text refers to this axis. This assumption is necessary, to perform the analysis in terms of the theoretical models described in § 2, and it is commonly accepted in the literature for such analysis [2, 20].

The fitting results for the SmC* phase correspond to a very good agreement between experimental and calculated spectral densities, comparable with that obtained for the SmA and uSmC* phases (see figure 3). The assumption of a single Arrhenius trend for diffusion coefficients in the SmA and uSmC* phases is also supported by the substantial lack of discontinuity (within the experimental uncertaintees) between the two mesophases. The good agreement between experimental and calculated experimental densities in the temperature range of stability of the SmA and uSmC* phases also supports our assumptions.

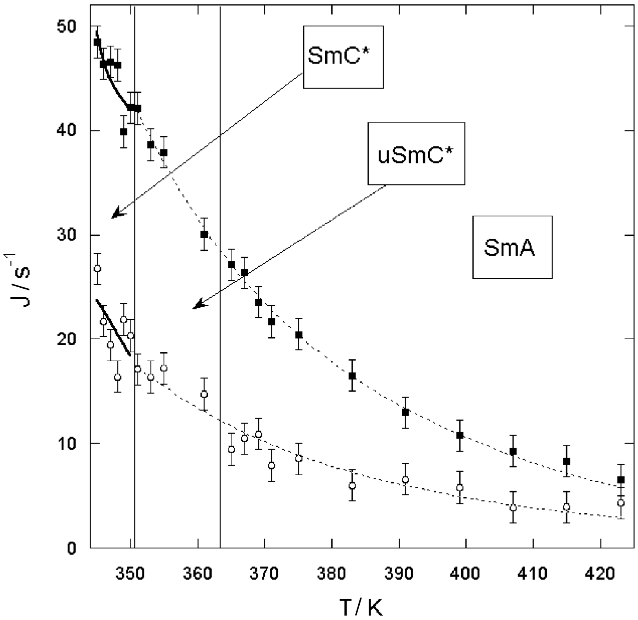

Figure 3. Experimental (symbols) and calculated (lines) spectral densities of MBHB-d$_8$ in the SmA, uSmC* and SmC* phases vs. temperature. Full squares and empty circles refer to $J_1(\omega_0, \theta)$ and $J_2(2\omega_0, \theta)$, respectively.

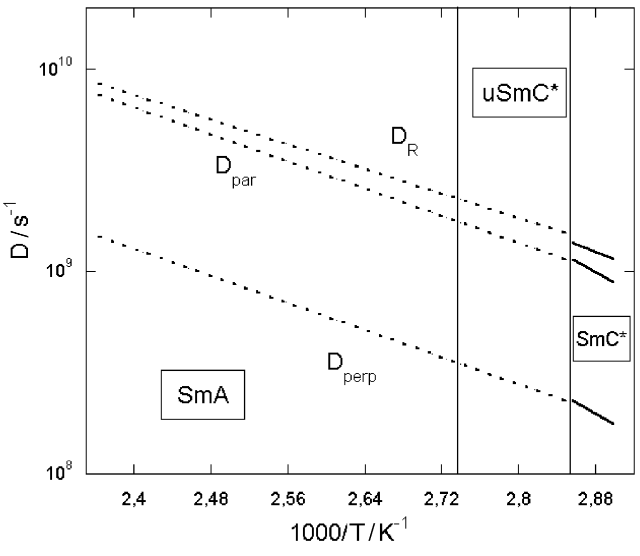

Figure 4. Diffusion coefficients of MBHB-d$_8$ relative to spinning ($D_{\mathrm{par}}$), tumbling ($D_{\mathrm{perp}}$) and internal rotation of the biphenyl ring ($D_{\mathrm{R}}$) reported in a logarithmic scale vs. 1000/*T* in the smectic phases.

The best-fitting parameters obtained for all phases are affected by relatively small errors (about 6% and 1% for pre-exponential factors and activation energies, respectively) and the corresponding diffusion coefficients are reported in figure 4. In the trends of all the diffusion coefficients, the changes at the uSmC*–SmC* transition are largely within the experimental errors, thus indicating the absence of a significant discontinuity in both internal and overall motions also on entering the tilted SmC* phase.

A difference between SmC* and uSmC*–SmA phases is seen in the activation energies for the overall molecular motions (increasing from 32 to 52 kJ mol$^{-1}$ going from the SmA–uSmC* to the SmC* phase), and, to a minor extent, for the internal rotation of the biphenyl fragment (slightly increasing from 29 to 36 kJ mol$^{-1}$).Comparing these results with literature results for other ferroelectric samples, in the present case we could observe an increase in the activation energy for the overall and internal motions on passing from the aligned to the tilted smectic phase. A similar trend has been reported in the literature, even though in this case the increase was smaller than in other ferroelectric liquid crystals [8, 9, 19]. Moreover, in respect to the case of 11EB1M7 [19], we could observe no significant jump in the diffusional coefficient describing the tumbling motion at the transition. However, small discontinuities at the SmC*–uSmC* transition can be observed in the trend of $J_2$ and in the slope of calculated $J_1$ and $J_2$ as a function of temperature (see figure 3).

This behaviour was reproduced by the calculated spectral densities. Similar fittings, performed using the small step rotational diffusion model instead of strong collision for internal ring rotations, gave a much worse agreement with experimental data, confirming previous results obtained for other ferroelectric smectogens [30–32]. This behaviour was found to be peculiar for ferroelectric smectogens in contrast to non-ferroelectric smectogens [23, 33].

## 5. Conclusions

Although the analysis of dynamics in uniaxial phases, such the SmA, is still very important for testing theoretical models and for a comparison of different spectroscopic techniques, the study of the dynamics in the SmC* phase here reported is an important contribution to the understanding of dynamics in liquid crystals. The experimental and theoretical problems connected with the analysis of relaxation times in the ferroelectric phase when considering both the azimuthal angle and its biaxiality, have been overcome by introducing an approximation, which allows the use of existing models by neglecting the azimuthal dependence of the measured relaxation times. The ferroelectric smectogen MBHB has been studied in its SmC* phase by using this approximation. Relaxation data in the SmA and uSmC* phases have also been analysed, using standard uniaxial models.

The comparison between the results here reported in the SmC* phase and those obtained in the SmA and uSmC* phases shows that there are no significant discontinuities at the SmA–uSmC*–SmC* transition except for a small discontinuity in $J_2$ at the uSmC*–SmC* transition. On the other hand, the activation energies of the diffusion motions increase on passing from the SmA–uSmC* to the SmC* phase. This behaviour confirms the general trend observed in other ferroelectric smectogens, revealing that no significant changes occur in the fast regime of motions.

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